



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 333 037
A2**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 89104197.2

(51) Int. Cl.4: C01B 3/40 , B01J 23/46

(22) Date of filing: 09.03.89

(30) Priority: 12.03.88 JP 59165/88
04.08.88 JP 194751/88
04.08.88 JP 194752/88

(43) Date of publication of application:
20.09.89 Bulletin 89/38

(84) Designated Contracting States:
BE CH DE FR GB IT LI NL SE

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(54) Catalyst for steam reforming of hydrocarbon.

(57) The present invention provides a catalyst for steam reforming of hydrocarbons which comprises ruthenium supported on a zirconia carrier; and a catalyst for steam reforming of hydrocarbons which comprises (A) at least one element selected from the group consisting of rhodium and ruthenium as an element imparting mainly reforming activity and (B) at least one element selected from the group consisting of nickel, lanthanum, praseodymium, neodymium, samarium, thorium, uranium, chromium, magnesium, calcium, and yttrium as an element for imparting co-catalyst function which are supported on a zirconia carrier; and furthermore a catalyst for steam reforming of hydrocarbons which comprises at least one element selected from the group consisting of rhodium and ruthenium which is supported on a partially stabilized zirconia carrier.

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- a catalyst for steam reforming of hydrocarbons (catalyst I) which is characterized by comprising a zirconia carrier on which ruthenium is supported;
- a catalyst for steam reforming of hydrocarbons (catalyst II) which is characterized by comprising a zirconia carrier on which are supported (A) at least one metal selected from the group consisting of rhodium and ruthenium as an element to impart mainly reforming activity and (B) at least one element selected from the group consisting of nickel, lanthanum, praseodymium, neodymium, samarium, thorium, uranium, chromium, magnesium, calcium and yttrium as an element to impart co-catalyst function; and
- a catalyst for steam reforming of hydrocarbons (catalyst III) which is characterized by comprising a partially stabilized zirconia carrier on which is supported at least one element selected from the group consisting of rhodium and ruthenium.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

(1) Catalyst I:

Zirconia carrier:

- It is especially important that zirconia is selected as a carrier in the present invention. This is because this zirconia carrier is especially high in reactivity with water, performs improvement of ability to reform hydrocarbons with steam and restrains deposition of carbon on the catalyst.
- Such zirconia carrier includes zirconium oxide and a substance capable of being converted to zirconium oxide at the time of preparation of catalyst or at steam reforming.
- The above zirconium oxide may be commercially available one.
- As the substance capable of being converted to zirconium oxide at the time of preparation of catalyst or at steam reforming, mention may be made of, for example, zirconium hydroxide, zirconium halide, zirconium nitrate, zirconyl nitrate, zirconium acetate, zirconium oxalate, zirconium alkoxide, zirconium oxychloride and organozirconium compound.
- Sparingly soluble salts may be solubilized and used by adding, for example, an acid.
- The above various zirconium compounds may be used alone or in combination of two or more.
- Among them, zirconyl nitrate is especially preferred.
- When zirconyl nitrate is used, zirconium oxide can be prepared by subjecting zirconyl nitrate to precipitation with ammonia water and thermally decomposing the precipitate. This may also be prepared by hydrolysis of an alkoxide compound of zirconium.
- The zirconium oxide used as a carrier may be anhydrous or may contain water of crystallization.
- Most preferred is zirconium oxide.
- In the present invention, other carriers may also be used together with the aforementioned zirconium compounds as zirconia carriers as far as attainment of the object of the present invention is not obstructed.
- Other carriers include silica, alumina and zeolite.
- The above-mentioned zirconium compounds and other carriers can be used as mixtures, or compositions such as composite oxides or composites comprising said zirconium compounds supported or coated on other carriers. Shape of the zirconia carrier is not critical and may have optional shapes such as fine powders, beads, pellets, plates, films and monolith.

Metal to be supported; ruthenium:

- As ruthenium sources for supporting ruthenium, mention may be made of, for example, ruthenium halides such as ruthenium iodide and ruthenium chloride, haloruthenates such as ammonium chlororuthenate, haloruthenic acids such as chlororuthenic acid, ruthenium oxides such as ruthenium hydroxide, ruthenium dioxide and ruthenium tetraoxide, ruthenates such as potassium ruthenate and organic ruthenium compounds such as ruthenium carbonyl.
- Such ruthenium sources may be used alone or in combination of two or more.
- Amount of ruthenium supported is generally 0.1-5% by weight, preferably 0.3-3% by weight of zirconia carrier.
- In this case, if amount of ruthenium is too much, the carrier is covered with the supported metal and

Elements used as those of group (B):

As nickel sources for supporting nickel, mention may be made of, for example, nickel chloride (hexahydrate), nickel chloride (anhydride), nickel bromide (hexahydrate), nickel bromide (anhydride), nickel iodide (hexahydrate), nickel iodide (anhydride), nickel nitrate, nickel sulfate, nickel acetate, nickel formate, nickel oxalate, nickel hydroxide, nickel oxide, nickel carbonate, nickel acetylacetonate and nickel carbonyl.

Lanthanum sources, praseodymium sources, neodymium sources, samarium sources, chromium sources, uranium sources, thorium sources, magnesium sources, calcium sources, or yttrium sources for supporting lanthanum, praseodymium, neodymium, samarium, chromium, uranium, thorium, magnesium, calcium or yttrium include nitrates, sulfates, carbonates, acetates, hydroxides, oxides, basic salts, alkoxides and organic compounds of these metals.

These sources may be used alone or in combination of two or more.

Amount of element of group (B) obtained from the above metal sources can vary depending on kind of metal and cannot be indiscriminately specified, but normally 0.1-10% by weight, preferably 0.3-5% by weight of metals supported.

Preparation of catalyst:

Process for preparation of catalyst II is similar to that for catalyst I and has no special limitation. One suitable example of preparation of catalyst II is shown below.

That is, zirconium oxide is fired in the same manner as in preparation of catalyst I and the resulting fired product is dipped in a solution or a colloidal dispersion containing compounds of elements selected from group (A) and (B) and is treated in the same manner as in preparation of catalyst I to obtain a catalyst for steam reformation.

The fired product of zirconium oxide may be dipped in a solution or a colloidal dispersion of compounds of elements of group (A) and then in a solution or a colloidal dispersion of compounds of elements of group (B) or vice versa.

(3) Catalyst (III):

Partially stabilized zirconia carrier:

It is especially important that a partially stabilized zirconia carrier is selected as a carrier in the present invention.

This is because this partially stabilized zirconia carrier has inherited excellent properties as carrier such as especially high reactivity of zirconia per se with water, enhancement of ability to reform hydrocarbons with steam and prevention of deposition of carbon on catalyst and in addition to these properties, it is excellent in properties specific to partially stabilized zirconia resulting from addition of a stabilizer, namely, heat resistance and mechanical strength and is little in reduction of surface area even under a high temperature of at least 500 °C and can be stably used.

Such partially stabilized zirconia carrier can be obtained by modifying and stabilizing zirconia component with addition of a stabilizer.

Zirconium source used as raw material for zirconia component of this partially stabilized zirconia carrier includes zirconium oxide and substances capable of being converted into zirconium oxide (zirconia component) at the time of preparation of catalyst or at steam reforming.

The above zirconium oxide is the same as in catalyst I.

Zirconium alkoxide is especially preferred as zirconium source in catalyst III.

As stabilizers used as components of the partially stabilized zirconia carrier, mention may be made of, for example, yttrium oxide component, magnesium oxide component, cerium oxide component and other known various oxide components used as stabilizing components for so-called stabilized zirconia used in various fields of materials.

Among them, especially preferred are yttrium oxide component, magnesium oxide component and cerium oxide component.

These yttrium oxide component, magnesium oxide component and cerium oxide component can be formally expressed by Y_2O_3 , MgO and CeO_2 , respectively.

That is, the partially stabilized zirconia carrier obtained above is dipped in a solution or a colloidal dispersion of the above-mentioned ruthenium compound and/or rhodium compound normally for about 0.1-10 hours, preferably 0.5-5 hours, followed by mixing or kneading and evaporating to dryness. Then, the product is dried at 100-200°C for 0.1-24 hours and then fired at 500-850°C for 0.1-20 hours in air or nitrogen stream and, if necessary, molded into a desired shape, for example, by a tablet compressing method, followed by reduction treatment to obtain the catalyst for steam reforming of the present invention.

Steam reforming of hydrocarbon:

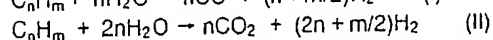
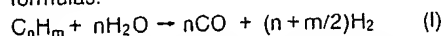
The above-mentioned catalyst I, catalyst II and catalyst III which are catalysts for steam reforming are used for accelerating steam reforming of hydrocarbons.

The hydrocarbons to be reformed are not limitative and include, for example, straight chain or branched chain saturated aliphatic hydrocarbons such as methane, ethane, propane, butane, pentane, hexane, heptane, octane, nonane, and decane and cycloaliphatic saturated hydrocarbons such as cyclohexane, methylcyclohexane and cyclooctane.

These hydrocarbons are used alone or in combination of two or more or may be various purified petroleum fractions.

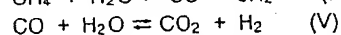
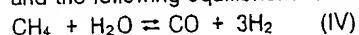
Steam to be reacted with hydrocarbons is not limitative.

The above hydrocarbons are considered to react with steam in accordance with the following reaction formulas.



[n in the formulas (I) and (II) represents a real number of 1 or more and m represents a real number of 2 or more.]

In addition to the above formulas, reaction (III) of formation of CH₄ by hydrogenolysis of hydrocarbon and the following equilibrium reactions can be considered to occur jointly..



Therefore, theoretically, amounts of hydrocarbon and steam used can be determined in stoichiometric amounts which satisfy the above reaction formulas (I)-(V), but when the catalyst of the present invention is used, amounts of hydrocarbon and steam are preferably determined so that the steam/carbon ratio is 3-12, preferably 3-8.

By employing such steam/carbon ratio, gases rich in hydrogen can be efficiently and stably obtained. Reaction temperature is normally 300-950°C, preferably 400-850°C.

It is worth notice that the catalyst of the present invention has sufficiently high catalytic activity even at a reaction temperature of 500°C or lower.

Reaction pressure is normally 0-50 kg/cm²G, preferably 0-20 kg/cm² G.

Reaction method may be any of continuous flowing method, batch method, and the like, but the continuous flowing method is suitable.

When the continuous flowing method is employed, gas space velocity (GHSV) of mixed gas of hydrocarbon and steam is usually 1,000-40,000 h⁻¹, preferably 2,000-20,000 h⁻¹.

What is worth notice when the catalyst of the present invention is used is that continuous operation is possible even at such high gas space velocity.

Reaction type is not limitative and may be any of fixed bed type, moving bed type, fluidized bed type, etc.

Type of reaction apparatus is also not limitative and, for example, a tube type reactor may be employed.

In this way, when hydrocarbon and steam are allowed to react in the presence of the catalyst of the present invention, the reaction proceeds normally and mainly in accordance with the above reaction formula (I), but since the reaction of the reaction formula (II), the equilibrium reaction (V) where produced carbon monoxide and water react to produce carbon dioxide and hydrogen and the equilibrium reaction (IV) where carbon monoxide and hydrogen react to produce methane and water also take place simultaneously, as a result there is obtained a mixture of hydrogen, methane, carbon monoxide and carbon dioxide, although main product is hydrogen.

The resulting mixed gas can be used as it is or can be separated into respective gas components, which are used for respective purposes.

The present invention is explained by the following examples.

The results are shown in Table 2.

Comparative Example 2

Procedure of Examples 14-15 was repeated except that Rh/ZrO was used as a catalyst.

Table 2

	Catalyst system	Total conversion rate (%)	
		Initial	After 1,000 hr
Example 14	Rh-Th/ZrO ₂	68.2	68.1
Example 15	Rh-La/ZrO ₂	61.0	60.5
Comparative Example 2	Rh/ZrO ₂	50.7	47.0

Examples 16-20

Preparation of partially stabilized zirconia carrier:

Zirconium alkoxide as zirconium source for zirconia component (formally ZrO₂) and an alkoxide of yttrium, magnesium or cerium as yttrium source, magnesium source or cerium source for yttrium oxide component (formally Y₂O₃), magnesium oxide component (formally MgO) or cerium oxide component (formally CeO₂) were respectively dissolved in isopropyl alcohol and water was added thereto with well stirring to effect hydrolysis to precipitate a composite oxide (hydrate) of large surface area comprising ultrafine particles of 0.03 μ m in primary particle size. The resulting precipitate was washed, then dried at 120 °C for 24 hours and thereafter, fired for 3 hours in air to obtain a partially stabilized zirconia carrier having a composition desired as a carrier for partially stabilized zirconia supporting catalysts as shown in Table 3.

Preparation of catalyst:

On the partially stabilized zirconia carrier was supported RuCl₃ or RhCl₃ in an amount of 0.5% by weight in terms of metal, followed by reducing treatment with hydrogen in a reaction tube to prepare steam reforming catalyst supported on the partially stabilized zirconia as shown in Table 3.

Using the catalyst obtained above, steam reforming was carried out by normal-pressure fixed bed flow type reaction apparatus using n-butene as a starting material and employing the reaction conditions of reaction temperature: 450 °C, reaction time factor: 622.7 (g-cat min./n-butane mol) and steam/carbon ratio of 12 (feeding ratio of steam and n-butane calculated from molar ratio).

Continuous analyses by a gas chromatography gave the results as shown in Table 3 on catalyst activity (total conversion rate) after 10 hours from initiation of the reaction and composition of the resulting gas (carbon monoxide, methane, carbon dioxide and hydrogen).

Comparative Example 3

The catalyst Rh/ZrO₂ shown in Table 3 was obtained by supporting RhCl in an amount of 0.5% by weight of rhodium supported on ZrO carrier prepared by firing ZrO₂ · xH₂O at 500 °C for 1 hour in air.

Reaction was carried out in the same manner as in Example 16 using the Rh/ZrO₂ catalyst.

The results are shown in Table 3.

Table 4

	Catalyst system	Total conversion rate (%)		Pressure loss of catalyst layer (relative value)		Surface area of catalyst (m^2/g)	
		Initial	After 1000 hr	Initial	After 1000 hr	Initial	after 1000 hr
Comparative Example 4	Rh/ZrO ₂	50.7	47.0	1.0	2.2	60	20
Example 21	Rh/partially stabilized ZrO ₂ (1)	67.0	65.8	1.0	1.3	70	45

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04.08.88 JP 194751/88
04.08.88 JP 194752/88

(43) Date of publication of application:
20.09.89 Bulletin 89/38

(84) Designated Contracting States:
BE CH DE FR GB IT LI NL SE

(88) Date of deferred publication of the search report:
01.08.90 Bulletin 90/31

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neodymium, samarium, thorium, uranium, chromium, magnesium, calcium, and yttrium as an element for imparting co-catalyst function which are supported on a zirconia carrier; and furthermore a catalyst for steam reforming of hydrocarbons which comprises at least one element selected from the group consisting of rhodium and ruthenium which is supported on a partially stabilized zirconia carrier.

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